Thermodynamic Equilibrium between Melt and Crystalline Phase of a Compound $\mathrm{A}_q\mathrm{B}_r$ with Dystectic Melting Point
I. Theoretical Approach

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Received 10 May 1999

To describe the equilibrium between the crystalline phase and melt in the system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$, when the substance $\mathbf{A}_q\mathbf{B}_r$ partially dissociates upon melting, the special form of the LeChatelier—Shreder equation was derived without assuming any hypothetical equilibrium states and the occurrence of any hypothetical thermodynamic quantities. To fit both the phase and the chemical equilibrium in the system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$, an original method for the calculation of the values of the degree of dissociation of the compound $\mathbf{A}_q\mathbf{B}_r$ in the melt, the heat of fusion at dystectic temperature of fusion, and the dissociation enthalpy using this equation was proposed.

In some binary salt systems $\mathbf{A}$—$\mathbf{B}$ the binary compounds $\mathbf{A}_q\mathbf{B}_r$, partially dissociating upon melting with products being the constituents A and B, may be formed. In the molten state these compounds may exhibit sometimes a lowered symmetry of the coordination sphere of the central atom of the complex anion, sometimes they form associates bound by van der Waals forces. Owing to this fact and obviously a relatively higher energetic state such compounds undergo often at melting a more or less extended thermal dissociation, in some cases they melt even incongruently. Evidences of such behaviour may be found *e.g.* in [1, 2]. Due to the thermal dissociation, the liquidus curve of the compound $\mathbf{A}_q\mathbf{B}_r$ in the system $\mathbf{A}$—$\mathbf{B}$ exhibits at the temperature of fusion a curvature [3] the radius of which depends on the degree of dissociation of the compound $\mathbf{A}_q\mathbf{B}_r$. The higher is the dissociation degree, the flatter is the liquidus curve.

The classical approach to the calculation of the liquidus curve of $\mathbf{A}_q\mathbf{B}_r$, suggested *e.g.* by *Kremann* [4], *Roozeboom* and *Aten* [5], *Grjotheim et al.* [6], and *Hatem et al.* [7], uses as the standard state the nondissociated compound $\mathbf{A}_q\mathbf{B}_r$ and is based on some simplifying assumptions. This approach considers implicitly that the dissociation enthalpy of $\mathbf{A}_q\mathbf{B}_r$ is equal to zero. Moreover, the calorimetric enthalpy of fusion of $\mathbf{A}_q\mathbf{B}_r$, which is frequently inserted into the LeChatelier—Shreder equation, is commonly measured at the experimental temperature of fusion of $\mathbf{A}_q\mathbf{B}_r$ and not at the hypothetical temperature of fusion of the nondissociated compound. Thus it involves also the dissociation enthalpy.

The aim of this paper is to describe the coexistence of the crystalline substance $\mathbf{A}_q\mathbf{B}_r$ with its melt using procedure which does not assume any hypothetical equilibrium state. It leads to the special form of the LeChatelier—Shreder equation without the presence of any hypothetical thermodynamic quantity. In addition, this equation will be used to calculate the values of the degree of dissociation of the compound $\mathbf{A}_q\mathbf{B}_r$ in the melt, its heat of fusion by fitting the liquidus curves of the $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$ phase diagram and – in particular cases – of the dissociation enthalpy. A brief description of the calculation procedure is also included.

THEORETICAL

LeChatelier—Shreder Equation for Binary Systems Involving Compounds with Dystectic Melting Point

Let us consider a molten system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$ (Fig. 1) being at all temperatures in chemical equilibrium. (The components of the binary system are denoted in bold, the ones of the ternary system (*i.e.* "the constituents") in regular.)

The equilibrium coexistence of the crystalline substance $\mathbf{A}_q\mathbf{B}_r$ with the melt in the system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$, in which the compound $\mathbf{A}_q\mathbf{B}_r$ in the liquid phase partially dissociates to the constituents A and B at temperature T according to the reaction scheme

$$\mathrm{A}_q\mathrm{B}_r \Leftrightarrow q\mathrm{A} + r\mathrm{B} \qquad (1) \qquad (A)$$

is described by the relation

$$\mu^\circ(\mathbf{A}_q\mathbf{B}_r, \mathrm{cr}, T) = \mu(\mathbf{A}_q\mathbf{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) =$$

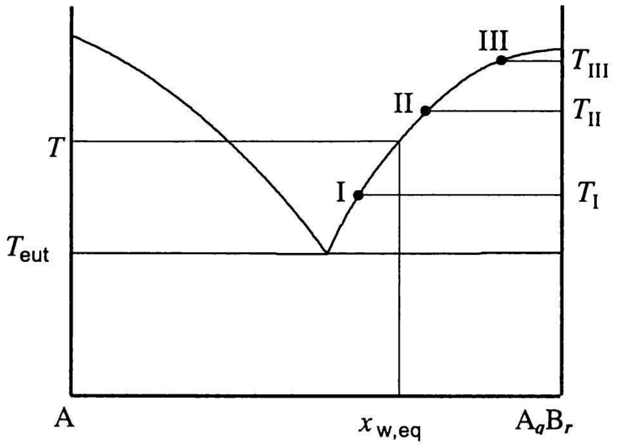

Fig. 1. Phase diagram of a system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$ with dystectic temperature of fusion. T_{I}, T_{II}, and T_{III} are the temperatures of the crystallization at the figurative points I, II, and III on liquidus curve of $\mathbf{A}_q\mathbf{B}_r$.

$$\begin{gathered}= [1 - \alpha_{(A)}(T)] \cdot \mu(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) + \\ + \alpha_{(A)}(T) \cdot q \cdot \mu(\mathrm{A}, \mathrm{l}, x_{\mathrm{w,eq}}, T) + \\ + \alpha_{(A)}(T) \cdot r \cdot \mu(\mathrm{B}, \mathrm{l}, x_{\mathrm{w,eq}}, T) \qquad (1)\end{gathered}$$

where $\mu^{\circ}(\mathbf{A}_q\mathbf{B}_r, \mathrm{cr}, T)$ is the chemical potential of the pure crystalline substance $\mathbf{A}_q\mathbf{B}_r$ at the temperature T, x_{w} is the weighted-in mole fraction of the component $\mathbf{A}_q\mathbf{B}_r$ in the $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$ system (*i.e.* $x(\mathbf{A}_q\mathbf{B}_r)$), $\mu(\mathbf{A}_q\mathbf{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T)$ is the chemical potential of the into equilibrium dissociated substance $\mathbf{A}_q\mathbf{B}_r$ in the molten mixture at the composition $x_{\mathrm{w,eq}}$ and the temperature T, $\mu(\mathrm{X}, \mathrm{l}, x_{\mathrm{w,eq}}, T)$ ($\mathrm{X} = \mathrm{A}_q\mathrm{B}_r$, A, B) is the chemical potential of the constituent X in the molten mixture at the same composition and temperature, and $\alpha_{(A)}(T)$ is the equilibrium degree of dissociation reaction (A) in the molten mixture at the temperature T; subscript $_{\mathrm{eq}}$ denotes quantities related to the phase equilibrium.

The condition for the assumed chemical equilibrium of the reaction (A) is given by the relation for the dissociation Gibbs energy

$$\begin{gathered}\Delta_{\mathrm{dis}}G(\mathrm{l}, x_{\mathrm{w}}, T) = q \cdot \mu(\mathrm{A}, \mathrm{l}, x_{\mathrm{w}}, T) + \\ + r \cdot \mu(\mathrm{B}, \mathrm{l}, x_{\mathrm{w}}, T) - \mu(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w}}, T) = 0 \qquad (2)\end{gathered}$$

Substituting eqn (2) for $x_{\mathrm{w}} = x_{\mathrm{w,eq}}$ into eqn (1), it can be rewritten in the form

$$\begin{gathered}\mu^{\circ}(\mathbf{A}_q\mathbf{B}_r, \mathrm{cr}, T) = \mu(\mathbf{A}_q\mathbf{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) = \\ = \mu(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) \qquad (3)\end{gathered}$$

In the following text the quantities corresponding to the pure, into equilibrium dissociated substance $\mathbf{A}_q\mathbf{B}_r$ ($x_{\mathrm{w}} = 1$) at the considered temperature T will be denoted by the subscript $_+$.

The chemical potential of $\mathrm{A}_q\mathrm{B}_r$ in the molten mixture can be expressed in the form

$$\begin{gathered}\mu(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) = \mu_{+}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T) + \\ + RT \ln \boldsymbol{a}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) \qquad (4)\end{gathered}$$

where $\mu_{+}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T)$ is the standard chemical potential of the nondissociated constituent $\mathrm{A}_q\mathrm{B}_r$ being at temperature T in the melt in chemical equilibrium with its dissociation products. According to eqn (3) the value of $\mu(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T)$ corresponds to that of the pure, partially dissociated molten substance. $\boldsymbol{a}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T)$ is the activity of $\mathrm{A}_q\mathrm{B}_r$ referred to the mentioned standard state in a molten mixture at the composition $x_{\mathrm{w,eq}}$ and the same temperature.

Substituting from eqn (4) into eqn (3), we obtain

$$\begin{gathered}\mu^{\circ}(\mathbf{A}_q\mathbf{B}_r, \mathrm{cr}, T) = \mu_{+}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T) + \\ + RT \ln \boldsymbol{a}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T) \qquad (5)\end{gathered}$$

Dividing both sides of eqn (5) by ($-T$), *i.e.* transforming the chemical potentials into the corresponding Planck's functions, and differentiating according to T we obtain the LeChatelier—Shreder equation (both standard chemical potentials are differentiated at constant composition $x_{\mathrm{w}} = 1$)

$$\left[\frac{\partial \ln \boldsymbol{a}(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_{\mathrm{w,eq}}, T)}{\partial T}\right]_p = \frac{\Delta_{\mathrm{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T)}{RT^2} \qquad (6)$$

where $\Delta_{\mathrm{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T)$ is the experimentally, *i.e.* calorimetrically or cryometrically, measurable enthalpy of fusion of the substance $\mathbf{A}_q\mathbf{B}_r$ being partially dissociated in the melt according to the scheme (A) at the temperature T

$$\begin{gathered}\Delta_{\mathrm{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T) = \Delta_{\mathrm{fus}}H(\mathrm{A}_q\mathrm{B}_r, T) + \\ + \alpha_{(A),+}(T) \cdot \Delta_{\mathrm{dis}}H_{(A),+}(T) \qquad (7)\end{gathered}$$

where $\alpha_{(A),+}(T)$ is the dissociation degree according to the reaction (A) at temperature T. The activity in eqn (6) can be expressed using the definition relation

$$\boldsymbol{a} = \frac{f}{f_{+}} = \frac{\kappa p}{\kappa_{+} p_{+}} = \frac{\kappa k_{\mathrm{H}} x}{\kappa_{+} k_{\mathrm{H},+} x_{+}} = \frac{\dfrac{f}{f_0}}{\dfrac{f_{+}}{f_0}} = \frac{a}{a_{+}} \qquad (8)$$

where f, κ, p, k_{H}, and x denote the corresponding values of the fugacity, fugacity coefficient, equilibrium partial pressure, the Henry constant, and the true mole fraction of the considered substance. The true mole fraction of the i-th constituent we define as

$x_i = n_i/\sum n_i$ where n_i is the amount of substance of the i-th constituent. In other words, the true mole fraction is the mole fraction of a constituent in the pseudoternary A—B—A_qB_r system. (Index "0" corresponds to the fictive state of pure nondissociated molten substance A_qB_r.)

The fugacity of the substance in an ideal solution is proportional to its mole fraction over the whole concentration range provided temperature to be constant. The fugacity coefficients and Henry constants do not depend on composition in real solutions at constant temperature (taking into account also low values of fugacity) in a narrow concentration range.

For ideal solutions and real solutions having the composition close to the composition of the pure $\mathbf{A}_q\mathbf{B}_r$ melt in which reaction (A) reaches equilibrium ($x_\text{w} \to 1$, $T \to T_\text{fus}$), eqn (8) at constant temperature can therefore be expressed in the form

$$a(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_\text{w,eq}, T) = \frac{x(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_\text{w,eq}, T)}{x_+(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T)} \qquad (9)$$

The activity of A_qB_r is thus the ratio of the true mole fractions of A_qB_r in the molten mixture and in the melt of the pure dissociated substance $\mathbf{A}_q\mathbf{B}_r$ at the temperature T.

Inserting for $\Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T)$ in eqn (6)

$$\begin{aligned}&\Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T) = \\ &= \Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)) + \\ &+ \int_{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)}^{T} \left(\frac{\partial \Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T)}{\partial T}\right) \mathrm{d}T \qquad (10)\end{aligned}$$

and integrating we get after rearrangement

$$\begin{aligned}&\frac{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)\cdot T}{T - T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)}\left[\ln\frac{a(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_\text{w,eq}, T)}{a_+(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T)}\right] = \\ &= \frac{\Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T_\text{fus}(\mathbf{A}_q\mathbf{B}_r))}{R} + \\ &+ \frac{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)\cdot T}{T - T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} \cdot \qquad (11) \\ &\int_{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)}^{T} \frac{\int_{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)}^{T}\left(\frac{\partial \Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T)}{\partial T}\right)\mathrm{d}T}{RT^2}\mathrm{d}T\end{aligned}$$

For $T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)$ the second term on the right side of eqn (11) equals zero and for ideal solutions as well as for the real ones at the compositions close to the $\mathbf{A}_q\mathbf{B}_r$ melt eqn (11) can be rewritten using eqn (9) into the form

$$\begin{aligned}&\lim_{T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} \left\{ \left[\frac{T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)\cdot T}{T - T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)}\right] \cdot \right. \\ &\left. \cdot \left[\ln\frac{x(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_\text{w,eq}, T)}{x_+(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T)}\right] \right\} = \\ &= \lim_{T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} \Psi = \\ &= \frac{\Delta_\text{fus,exp}H(\mathbf{A}_q\mathbf{B}_r, T_\text{fus}(\mathbf{A}_q\mathbf{B}_r))}{R} = \text{const} \qquad (12)\end{aligned}$$

It can be exactly proved that from eqn (12) it follows

$$\lim_{T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} \frac{\mathrm{d}\Psi}{\mathrm{d}T} = 0, \text{ resp. } \lim_{x_\text{w,eq} \to 1} \frac{\mathrm{d}\Psi}{\mathrm{d}x_\text{w,eq}} = 0 \qquad (13)$$

The calculation of the unknown parameters represents the topic of the next chapter and is based on the special form of the modified LeChatelier—Shreder equation (12) as well as on relations (13).

Calculation of the Degree of the Dissociation Reaction (A) Using the Known Phase Diagram

In the calculation of $\alpha_{(A),+}(T_\text{fus}(\mathbf{A}_q\mathbf{B}_r))$ the following relations, obtained by means of the stoichiometric coefficients of reaction (A) and the value of the weighted-in equilibrium mole fraction $x_\text{w,eq}$, were used

$$x(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, x_\text{w,eq}, T) = \frac{(1 - \alpha_{(A)}(T))x_\text{w,eq}}{x_\text{w,eq}\alpha_{(A)}(T)\cdot(q + r - 1) + 1} \qquad (14)$$

$$x_+(\mathrm{A}_q\mathrm{B}_r, \mathrm{l}, T) = \frac{1 - \alpha_{(A),+}(T)}{\alpha_{(A),+}(T)\cdot(q + r - 1) + 1} \qquad (15)$$

$$x(\mathrm{A}, \mathrm{l}, x_\text{w,eq}, T) = \frac{x_\text{w,eq}(\alpha_{(A)}(T)\cdot q - 1) + 1}{x_\text{w,eq}\alpha_{(A)}(T)\cdot(q + r - 1) + 1} \qquad (16)$$

$$x_+(\mathrm{A}, \mathrm{l}, T) = \frac{\alpha_{(A),+}(T)\cdot q}{\alpha_{(A),+}(T)\cdot(q + r - 1) + 1} \qquad (17)$$

$$x(\mathrm{B}, \mathrm{l}, x_\text{w,eq}, T) = \frac{x_\text{w,eq}\alpha_{(A)}(T)\cdot r}{x_\text{w,eq}\alpha_{(A)}(T)\cdot(q + r - 1) + 1} \qquad (18)$$

$$x(\mathrm{B}, \mathrm{l}, T) = \frac{\alpha_{(A),+}(T)\cdot r}{\alpha_{(A),+}(T)\cdot(q + r - 1) + 1} \qquad (19)$$

$$\begin{aligned}K_{(A),a}(T) &= K_{(A),x}(T)\cdot K_{(A),\gamma}(T) = \\ &= K_{(A),x,+}(T)\cdot K_{(A),\gamma,+}(T) \qquad (20)\end{aligned}$$

$K_{(A),a}(T)$ is the equilibrium constant of the reaction (A) at the temperature T, $K_{(A),x}$, $K_{(A),\gamma}$, $K_{(A),x,+}(T)$, and $K_{(A),\gamma,+}(T)$ are the products of the respective mole fractions and activity coefficients of the constituents in the melt of the composition $x_\text{w,eq}$ and in the molten pure compound $\mathbf{A}_q\mathbf{B}_r$ (subscript $_+$), respectively.

From the validity of eqns (8) and (20) follow the limiting relations

$$\lim_{T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} K_{(A),\gamma}(T) = K_{(A),\gamma,+}(T) \qquad (21)$$

$$\lim_{T \to T_\text{fus}(\mathbf{A}_q\mathbf{B}_r)} K_{(A),x}(T) = K_{(A),x,+}(T) \qquad (22)$$

and thus

$$\lim_{T\to T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r)}\left[\frac{\partial \ln K_{(A),x}(T)}{\partial T}\right] =$$

$$= \left[\frac{\partial \ln K_{(A),x,+}(T)}{\partial T}\right] =$$

$$= \frac{\Delta_{\text{dis}}H^{\circ}_{(A)}(T) + \sum_i \nu_i \cdot \Delta_{\text{mix}}\overline{H}_{i,+}(T)}{RT^2} =$$

$$= \frac{\Delta_{\text{dis}}H_{(A),+}(T)}{RT^2} \qquad (23)$$

$\Delta_{\text{dis}}H^{\circ}_{(A)}(T)$ is the standard dissociation enthalpy of reaction (A), $\Delta_{\text{mix}}\overline{H}_{i,+}(T)$ and $\Delta_{\text{dis}}H_{(A),+}(T)$ is the partial molar enthalpy of mixing of the i-th constituent and the dissociation enthalpy of the pure compound $\mathbf{A}_q\mathbf{B}_r$ (ν_i is the stoichiometric coefficient).

In the calculation of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ the courses of the dependences of Ψ (eqn (*12*)) on $x_{\text{w,eq}}$ for different values of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ (and thus also $K_{(A),x,+,\text{eq}}$) are compared. Using $K_{(A),x,+}$ the value of $\alpha_{(A)}(T)$ in eqn (*14*) for the mole fraction $x(\text{A}_q\text{B}_r, \text{l}, x_{\text{w,eq}}, T)$ is calculated. The course of Ψ depends on the properties of the considered system. (The more detailed course of estimation of all quantities mentioned above and the analyses of the corresponding errors will be given in Part II.)

a) The melts form ideal solutions of constituents

At the given conditions ($a_i = x_i$; $\Delta_{\text{fus}}C_p(\text{A}_q\text{B}_r) = 0$; $\Delta_{\text{dis}}H_{(A)}(T) = \Delta_{\text{dis}}H_{(A),+}(T) = 0$) the following relation holds ($\text{d}p = 0$)

$$\frac{\partial \Delta_{\text{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T)}{\partial T} = 0 \qquad (24)$$

and eqn (*11*) transforms to the form

$$\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const}) =$$

$$= \frac{\Delta_{\text{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))}{R} = \text{const} \qquad (25)$$

For the correct value of $\alpha_{(A),+}(T)$ eqn (*25*) is the straight line parallel to the x_{w} axis.

b) The melts form ideal solutions of constituents at the conditions ($a_i = x_i$; $\Delta_{\text{fus}}C_p(\text{A}_q\text{B}_r) \neq 0$; $\Delta_{\text{dis}}H_{(A)}(T) = \Delta_{\text{dis}}H_{(A),+}(T) = 0$)

According to eqn (*11*) the graphical form of the function $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ is a curve fulfilling condition (*12*).

c) The melts form real solutions

If $\Delta_{\text{dis}}H_{(A),+}(T) \neq 0$, the quantities $\alpha_{(A),+}$ and $K_{(A),x,+}$ depend on temperature and the function $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ even in the case of ideal solutions has a formal character. However, in the vicinity of the dystectic point of fusion of $\mathbf{A}_q\mathbf{B}_r$ the temperatures of primary crystallization are only very little lowered and thus the values of $\alpha_{(A),+}$ and $K_{(A),x,+}$ keep practically constant. Thus for the given constant value of $\alpha_{(A),+}$ the course of the "formal" function Ψ in this region of compositions is identical with the real course of Ψ for ideal solutions as well as for real solutions and is represented by eqn (*12*).

According to the amount and reliability of information on the investigated system the procedure of the determination of the $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ value is as follows:

1. If the reliability of the course of the liquidus curve in the vicinity of $T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r)$ is insufficient, the knowledge of $\Delta_{\text{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ for the calculation of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ is unavoidable.

The course of $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ calculated using the coordinates of the figurative points of the reliable determined part of the liquidus curve for the chosen constant value of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ is described by suitable regression function. Such a function must be monotonous without any inflex point and it must fulfil the conditions (*12*) and (*13*).

2. If the dependence of the enthalpy of mixing on composition and temperature in the system $\mathbf{A}$—$\mathbf{A}_q\mathbf{B}_r$ is known, the values of $\Delta_{\text{fus}}H(\mathbf{A}_q\mathbf{B}_r, T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ and $\Delta_{\text{dis}}H_{(A),+}$ can be calculated.

3. If the course of the liquidus curve is sufficiently reliable in the whole temperature region, the course of $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ is described by regression function using the coordinates of all experimentally determined figurative points. The correct value of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ results in a function $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ which for $x_{\text{w,eq}} \to 1$ does not show either a maximum or an inflex point and it fulfils the conditions (*12*) and (*13*); the course of the function $\Psi(x_{\text{w,eq}}, \alpha_{(A),+}(T) = \text{const})$ in the vicinity of $T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r)$ depends on the stoichiometric coefficients q and r. In such a case together with the value of $\alpha_{(A),+}(T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ also the value of the enthalpy of the dystectic fusion $\Delta_{\text{fus,exp}}H(\mathbf{A}_q\mathbf{B}_r, T_{\text{fus}}(\mathbf{A}_q\mathbf{B}_r))$ can be calculated.

The application of the above procedures was made to the systems $\mathbf{KF}$—$\mathbf{K_3FMoO_4}$ and $\mathbf{KF}$—$\mathbf{K_3FWO_4}$ and is the subject of the second part of this paper.

Acknowledgements. This work was partially supported by the Scientific Grant Agency of the Slovak Ministry of Education and the Slovak Academy of Sciences under the No. 2/4032/98.

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